Application of MOFs in Lithium-Ion Batteries

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Abstract. In recent ten years, environmental pressure has been increasing, and the demand for batteries has been increasing, requiring high cycling capacity and large capacity clean batteries. This article introduces the research and application of metal–organic frameworks (MOFs) in lithium-ion batteries. This article also introduces the types and characteristics of MOFs, and explains the mechanism by which MOFs-based functional materials improve battery performance, such as enhancing electrode conductivity through the good conductivity of MOFs nanomaterials. The stable spatial structure of MOF materials brings more ion adsorption sites and changes in buffer electrode materials. Then, through the application of Co-MOFs materials in batteries, a brief introduction was given on the application of MOFs for negative electrode materials in lithium-ion batteries, demonstrating the superiority of MOFs as electrode materials. Finally, by introducing the characteristics of MOFs materials, the application of MOFs in batteries was prospected, and more design possibilities for MOFs materials were proposed.

Keywords: MOFs; Battery; Application.

1. Introduction

Lithium-ion batteries are a new battery system developed in the early 1990s. They have a variety of advantages, such as high voltage, good circulation performance, small self- discharge, etc. At present, nickel-cadmium batteries and nickel-hydrogen batteries are on the market, but the performance and production cost of lithium batteries are developing day by day. Its cost-effective advantages make it dominant in the field of mobile electronic terminal equipment and emerge in the energy of new energy vehicles. Although lithium-ion batteries have achieved great success in practical applications, they still have certain problems, such as poor cycling ability. To address this issue, the introduction of new porous functional materials, such as metal–organic frameworks (MOFs), into lithium-ion batteries has received increasing attention.

ZIF MOFs mainly use transition metals centered on zinc and cobalt, organic ligands such as imidazole and its derivatives as bridges, and synthesize MOFs materials through natural crystallization. Structurally similar to zeolite molecular sieves, it has high thermal stability and increases the variety of organic ligands used. It mainly consists of divalent copper ions as the central metal ions and heptyl benzoate as the organic ligand. It has stable pore size and excellent gas adsorption and storage capabilities.

Organic metal skeleton materials are mainly self-assembled materials with metal ions as the center and symmetric organic ligands such as dicarboxylic acids as connections. The length of organic ligands determines the pore size of MOFs, and the type of organic ligand determines the properties of MOFs. By replacing organic dicarboxylic acids of different lengths, MOFs materials be able to accurately adjust to meet different application requirements. At present, this type of material is divided into two categories: one is MOFs with "breathing phenomenon", which use transition metals as the central metal and dicarboxylic acid organic ligands such as succinic acid and glutamic acid as links, demonstrating flexibility in practical applications (pore size changes in material structure). Another method is to synthesize MOFs materials with complementary structures through group coordination, using valence transition metal ions as the center and carboxylic acid ligands as bridges. These materials have two different sizes of rigid pore structures.

Therefore, this research will mainly analyze how MOFs materials improve battery performance. Moreover, this research will also combine some practical examples for example analysis, which is expected to provide new ideas for the preparation and application of new porous materials.

2. How to improve electrodes with MOFs materials

2.1. Molecular sieving effect

MOFs materials can protect electrode materials and transport anions and cations through molecular sieve effect. The rapid development of modern society has led to environmental pollution, accelerated energy consumption, and increased resource waste, resulting in greater demand and stricter requirements for the growth of new energy storage methods and transform skills. Lithium ion batteries, as an efficient energy storage device, have always received attention from researchers, but there are still shortcomings such as decreased energy density, short cycle life, and poor safety performance. In order to meet the demand for lithium-ion batteries, researchers are developing functional electrolytes, additives, lithium electrodes and protection. MOFs, also known as porous coordination polymer, have periodic crystal structure, immearsurable network structure of metal ions and metal connected by organic ligands. Researchers can synthesize MOFs for specific purposes (e.g. gas separation, adsorption, storage, catalysis) by doping different metal ions, modifying the functional groups in the ligand and modifying the ligand type.

For example, MOFs material was used as ion sieve. In 2016, Bai et al. creatively used a prepared MOF as polylithium sulfide molecular sieve for the first time. The shuttle effect of Lithium sulfide will lead to the rapid decline of battery capacity and life. The formed lithium sulfide molecular sieve blocks the lithium sulfide with large molecular weight from remaining at the battery cathode, while allowing the free transmission of small molecules of lithium ions, which weakens the shuttle effect of lithium sulfide, indirectly improves the lithium ion transmission efficiency, and effectively improves the battery capacity and electrochemical stability [1]. In 2018, Zang et al. used a two-dimensional conductive layer $Ni_3(HITP)_2$ MOFs to prepare crack-free MOFs ion screen, which was used to restrain the shuttle of polylithium sulfide and improve the round constance and battery capacity. This molecular sieve also relies on the same principle to reduce the shuttle effect of lithium sulfide to improve the battery cycle efficiency and battery capacity [2]. In addition, MOFs materials are also used in the construction of battery combination electrolyte, negative electrode protection, quasi-solid electrolyte, etc. MOFs materials have good conductivity due to their central metal atoms. By doping with other substances, the electrode material exhibits more diverse chemical properties, thereby improving battery capacity and cycling rate. There is also a special spatial structure formed by MOF materials through their ligands, which can buffer the material and environmental changes brought about during battery use. The molecular sieves formed by the two MOFs materials have the same mode of action, leaving the macromolecular Lithium sulfide in the positive electrode area to reduce the shuttle effect of Lithium sulfide. The battery capacity and battery cycle stability have been improved due to the weakening of lithium sulfide shuttle effect.

2.2. Buffering deformation

Taking Co-MOFs materials as an example, cobalt sulfide is currently an ideal target for lithium storage. During the charging and discharging process of lithium-ion batteries, cobalt sulfide is mainly used as the negative electrode material [3]. Although it has high conductivity, (1) the electrode material may undergo pulverization due to volume changes, which affects the battery life. (2) On the other hand, cobalt sulfide is easily dissolved in the electrolyte, which increases the electrode impedance and leads to a decrease in specific capacity and a decrease in battery cycling stability. There are several main solutions to these two problems: (1) Preparation of porous or hollow nanomaterials, such as MOF materials, which have small volume and large specific surface area and good conductivity. This type of material has a hollow structure that can disperse cobalt sulfide particles, giving them more volume to adapt to electrode changes caused by charging and discharging processes. (2) The research on sulfide and carbon composite materials, as mentioned earlier, shows that pure MOFs have weak conductivity. If heteroatoms can be doped with carbon, they can change the charge distribution on the surface of the carbon material and serve as protective atoms to protect the material from corrosion, or to isolate the material to prevent agglomeration and sedimentation.

Why is MOF material said to have the potential as an electrode material? Here are some reasons. (1) The one-dimensional or two-dimensional structure of MOFs material can provide a specific surface area, so that more active site is exposed. Nanomaterials, due to their small volume, are beneficial for shortening the movement path of ions and electrons, improving ion and electron transport efficiency, and improving batteries performance. (2) During the long cycle process, the loss of electrode material often accompanies volume changes, and the layered porous structure can often fully buffer this volume change, which is conducive to the stability of electrode structure and cycle. (3) The special structure (porous and hollow morphology) increases the contact area in another way, shortening the diffusion pathway of lithium ions. (4) Bimetallic oxide composite materials. Different component materials work synergistically to store charges more effectively and shorten the lithium ion path. As shown in Fig. 1, Chen et al. prepared the hollow porous Octahedron composite material by heat treating the CoMo-MOFs material. As the battery cathode material, under the current density of 0.2 A/g, the average discharge specific capacity was 1175.1 mAh/g, and the capacity was still 96.9% after 100 cycles [4].

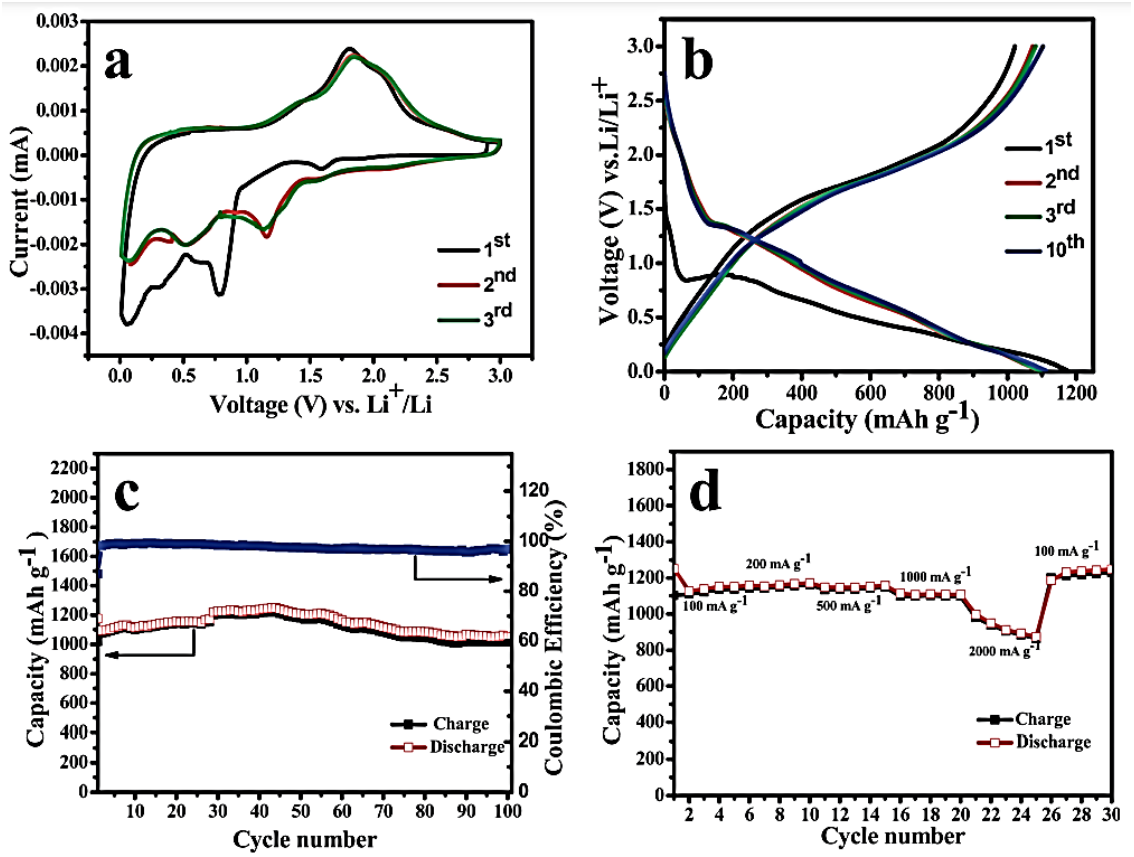


Fig 1. Electrochemical analysis of the prepared MOFs-based functional materials [4, https://pubs.rsc.org/en/content/articlelanding/2018/ta/c7ta08868j].

3. Modified

There are thousands of types of MOFs materials, and through the modification of their ligands, making them possess different properties has a good effect on improving battery performance. MOFs materials themselves also possess the properties of nanomaterials, with free electrons that can move freely on the central metal ions or metal clusters, which is more conducive to electron transfer and can be used as good conductive materials for battery electrodes. For example, in lithium batteries, the hexagonal nut like Ti MOFs synthesized by Xia et al. provides abundant redox sites to enable MOFs materials to have good cycling performance [5]. In addition, MOFs electrodes using carboxyl ligands have better specific capacity. On the one hand, because the carbon oxygen double bond on the carboxyl group has a conjugation effect, MOFs materials can have a more stable structure. On the

other hand, as an electrochemical Active site, carboxyl groups can be reversibly bonded with Li^+, and can also be ionic bonded with coo groups, so that the materials have high specific heat capacity. The Mn BTC MOF reported by Maiti et al. also verified that batteries with carboxylic acid ligand MOF as the negative electrode have good performance, exhibiting a high specific capacity of 694mAh/g at a current density of 0.1A/g. After 100 rounds, 83% of the specific capacity still shows good structural reversibility [6].

Generally speaking, pure MOF materials have poor conductivity, and when used as electrode materials, they can cause rapid and significant capacitance loss, resulting in energy loss. In order to improve battery efficiency, doping with other substances is often used. Doping substances can be of many types, such as heteroatoms (N, S, P, etc.), the second type metal elements, and second type MOFs, etc. By doping, MOFs materials can have more three-dimensional structures and more chemical properties. By doping various substances in this way, two different materials can enhance each other's performance or obtain more diverse properties, which can achieve ideal effect improvement. For example, as mentioned above, carboxylic acid ligands can provide more Active site binding.So using MOF materials has a good effect on improving battery performance.

Doped heteroatoms can be directly doped into MOFs derived materials through direct pyrolysis of MOF, and the type and quantity of doped heteroatoms can be selected by selecting the ligand type of MOF materials [7]. After doping with other elements, the application performance of MOFs materials will be further improved, which is more conducive to expanding their application range.

In batteries, good battery performance not only relies on good conductivity and high battery capacity, but also requires good cycling stability. The excellent cycling stability is often related to the electrode material of the battery, and whether there is any change in the surface area and structure of the battery electrode after a period of reaction. By doping modification, the performance of the battery can also be enhanced by improving its cycling ability. The skeleton structure of MOFs has good stability, which can buffer the stress changes caused by lithium removal and embedding, and maintain the structure of the battery electrode. The layered porous structure of MOFs materials can also buffer the volume expansion of electrode materials during cycling. The layered structure can also increase the contact area between electrolytes and active materials, reduce the diffusion distance of lithium ions, and there is a synergistic effect between multiple metal centers with different lithium storage sites between MOF materials, which has a good alleviating effect on the volume expansion caused by cycling. As shown in Fig. 2, Sun et al. used Fe/Zn MOF-74 porous hollow spherical structure Fe-Zn-S@S-C Composite materials, which rely on the synergy between iron disulfide and zinc sulfide [8]. The carbon matrix doped S provides the lithium active site, and the battery electrode expansion caused by the cycle process is further alleviated by the synergistic effect of carbon and sulfur. The electrode material exhibits excellent cycling stability. After more than 200 cycles, lithium-ion batteries still maintain good electrochemical performance. In addition, other functional MOFs functional materials have also been prepared and used to enhance the electrochemical performance of lithium-ion batteries [9, 10].

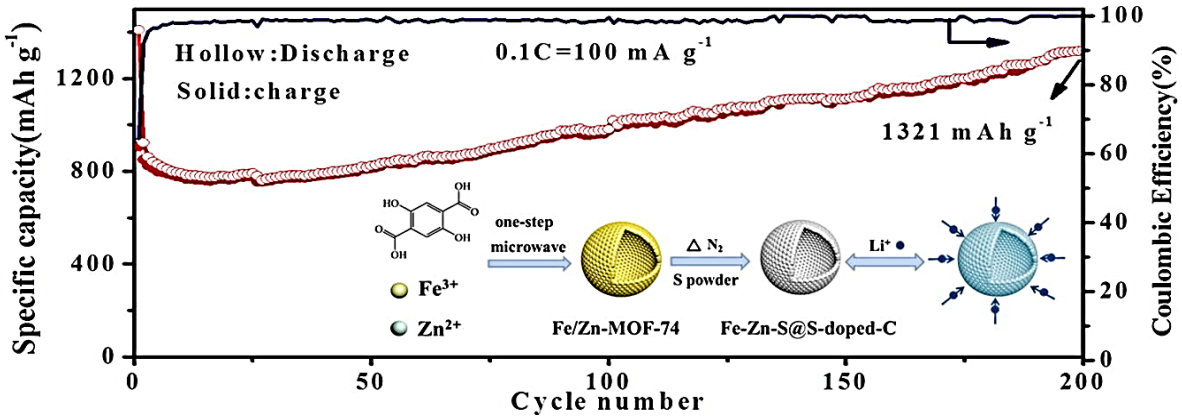


Fig 2. Lithium storage performance of MOFs functional materials [8, https://www.sciencedirect.com/science/article/pii/S1385894719302050].

4. Conclusion

This research mainly discusses the applications of different types of MOFs materials in the field of lithium-ion batteries, and explains the reasons why they are used to enhance the monetization of lithium-ion batteries. Regarding lithium-ion battery performance, it can be estimated through battery capacity, battery cycle stability, and rate. The application and development of MOFs-based functional materials in lithium-ion batteries are increasing, and they can be used as protective materials for electrodes to buffer electrode changes caused by charging and discharging processes, thereby extending lithium-ion battery life. It can be used as molecular sieve to help transport anions and cations, and reduce side effects such as lithium sulfide shuttle effect, so as to improve the maximum capacity and cycle stability of the lithium-ion battery. It can also be used as a good conductive material to enhance the conductivity of electrodes, promote electronic transportation, and thus improve battery efficiency. A variety of MOFs-based functional materials can often bring various performance improvements, and even further enhance battery capacity through modification of MOFs materials. There are many methods for modifying MOFs materials, such as doping heteroatoms, doping bimetals, doping double MOFs, and replacing ligand materials. MOFs materials have stable properties and a defined spatial structure. They cannot only protect the electrode and maintain the electrode structure through physical means, but also improve the performance and capacity of batteries through chemical means. By designing reasonable negative electrode materials for batteries, most of the problems found in current battery research can be solved. It should make more use of excellent modification methods such as molecular sieve effect, layered structure, and carboxylic acid ligands that have been discovered to design batteries that meet the needs of human life.

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